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The Mechanical Strength of Heterogeneous Catalyst

I. The Tensile Strength of Pelletized Alumina Catalysts

SHOKO YAMADAYA, MASAAKI OBA, TOJI HASEGAWA,
KIYOSHI OGAWA, AND YOSHIHIDE KOTERA

*Government Chemical Industrial Research Institute,
Tokyo, Mita, Meguro, Tokyo, Japan*

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Various alumina powders, prepared by the dehydration of alumina hydrate having a boehmite gel structure or bayerite structure were pelletized under different conditions. The mechanical strength, surface area, pore size distribution, and catalytic activity of the alumina pellets were measured. The strength of the pellets was affected by the water content in the powder and also by the heating temperature of the alumina powder, however it was not affected by the compacting pressure or time. Neither the surface area nor the catalytic activity of the aluminas is changed by pelletizing under the experimental conditions but the distribution of macropore volume does show some change.

Assuming that the Rumpf's relation can be used to explain the binding force in the agglomerates of the particles, the measured values of the tensile strength of the pellets correspond to the binding force exerted by the van der Waals' interaction between the adsorbed layers on the alumina particles.

INTRODUCTION

The preparation of catalysts for industrial use is carried out by various methods, however, scientific studies on the phenomenon occurring in this process have only been carried out in a few cases. The preparation of the pelletized catalyst from the powdered raw material is especially important in the application of solid catalysts for industrial use, and it is desirable from the practical standpoint to elucidate the dependence of the mechanical strength and catalytic activity on the pelletizing process. It is also interesting from the scientific standpoint to clarify the adhesion mechanism between the fine oxide particles. Rumpf (*1*) published a theoretical study on the mechanism of the occurrence of mechanical strength between fine particles in pellets; and recently, Turba and Rumpf (*2*) compared this theory with some experimental results. Experiments on the relation between the pelletizing action and the catalytic activity of some catalysts have also been reported (*3*).

In this study, alumina was used as a starting material, because (i) its physical properties have been studied in detail (*4, 5*), (ii) it is widely used as a catalyst and also as a carrier for industrial catalysts, and (iii) it is a typical oxide which is widely applied in the industry. Alumina was prepared by the reaction between sodium aluminate and aluminum sulfate solutions using a process previously reported (*5*), and was pelletized under various conditions. For the pellets thus prepared, measurements of the mechanical strength and pore size distribution were carried out, as well as measurement of the catalytic activity for some selected reactions.

It was possible to obtain some important information on the preparation process of the pelletized catalyst and also to examine the binding force between alumina particles in the pellets, assuming the model of Rumpf to be applicable to the agglomeration of the particles.

EXPERIMENTAL METHODS

Materials

The samples of alumina were prepared by the thermal decomposition of the alumina hydrate having a boehmite gel or bayerite structure. The hydrates were prepared by precipitation from aluminum sulfate solution by adding sodium aluminate solution under various conditions according to a previous paper (*5*). All preparations were carried out in a precipitation vessel with a stirrer for agitation. The aluminum salt solution and aluminate solution were mixed under definite temperature (15–60°C) and pH (9.8–8.5) conditions and the suspension obtained was aged at room temperature. The precipitates were filtered and washed with dilute aqua ammonia until the cake was freed from sulfate ion. The cake was then dried at 80°C in an oven. Each product was calcined at a definite temperature between 150 and 800°C for 3 hr.

Properties of Alumina

Aluminas and alumina hydrates were identified by an X-ray diffraction method, with a Geigerflex Diffractometer (Rigaku Denki Co.) using the Cu $K\alpha$ radiation.

Pore size distribution was measured by a mercury porosimeter (Carlo Erba AG-70), and the surface area was determined by the BET method from the adsorption isotherm of nitrogen.

The mean particle size of the samples was calculated by the assumption of cubic model from the surface area and the true density, the latter being determined by the mercury displacement method. The length of a side of the cube was defined as the particle diameter and these are the particle diameters used in Fig. 7. The catalytic activity of alumina samples for the isomerization of butene-1 was investigated by an ordinary flow apparatus with a microreactor.

Tableting Procedure

The samples in powder form were mixed with water (10 to 35% against those of sample wt) and were granulated by extrusion. The particles had an average diameter of about 0.5 mm and were dried until the desired water content was reached.

A given amount of the granules was compressed into a cyrindrical shape, 10 mm in diameter and 3.5 mm high using a die consisting of a stainless steel cylinder and a hardened chromium steel piston.

These pellets were calcined at 500°C for 3 hr, and stored in a desiccator.

Measurement of the Tensil Strength

The tensil strength was measured by using a "tensile test apparatus, SHIMAZU P-100." The measurement of pellet strength was carried out using a modification of Rumpf's method. Rumpf found that the main problem associated with the measurements of the mechanical strength of the pellet was to ensure that the pellet was suitably fastened and clamped. In the present work, stainless steel adaptors, 10 mm in diameter and 50 mm height, were used. The pellet was fastened by the adhesive "Alon Alpha" between the two adaptors. The mounted specimen was then fastened to the center of the upper and lower chucks of the tensile test apparatus. The apparatus and testing specimen are shown in Plate I. Measurements of the tensile strength of pellets made at various compacting times and pressures were carried out on five pellets tableted under the same compacting conditions. The minimum value obtained for the five pellets was taken as the tensile strength.

EXPERIMENTAL RESULTS

Properties of the aluminas are given in Table 1. The samples are classified into four groups according to their precipitation conditions.

The dependence of the tensile strength of the tablets on the compacting pressure is illustrated in Fig. 1. The strength increased with an increase in compacting pressure,

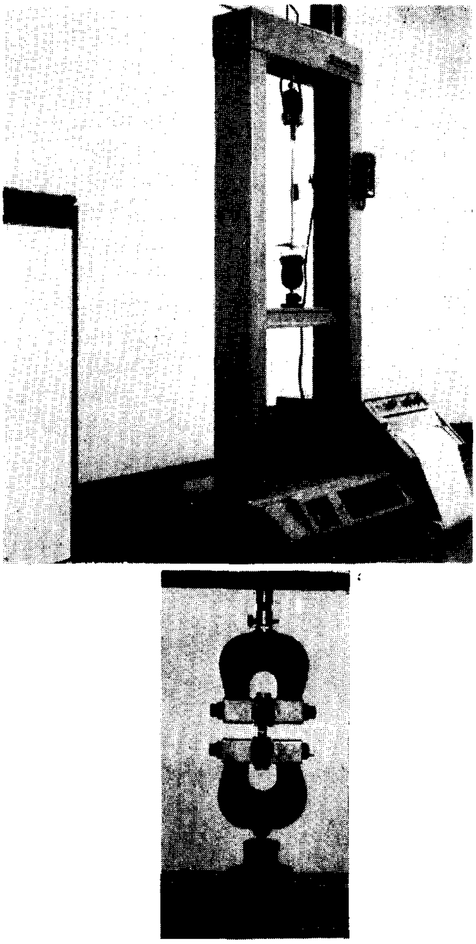

PLATE I. Tensile test apparatus and the sample for testing.

TABLE 1
PROPERTIES OF ALUMINAS AND ALUMINA HYDRATES

Sample	Thermal decomposition temp (°C)	Crystal phase[a]	Surface area[b] (m^2/g)
I-1	150	$B_{h\ gel} + B_y$	64
2	400	η or γ	318
3	600	η or γ	263
4	800	η or γ	125
II-1	150	$B_{h\ gel}$	298
2	500	η or γ	337
III-1	150	$B_{h\ gel}$	220
2	500	η or γ	245
IV-1	150	$B_{h\ gel}$	217
2	500	η or γ	326

[a] X-Ray analysis: $B_{h\ gel}$ = boehmite gel; B_y = bayerite; η = η- alumina; γ = γ-alumina.

[b] BET method.

until it reached a maximum value, where it remained constant.

For a definite pressure (6400 kg/cm²), the strength was independent of compacting time between 1 and 20 min, as shown in Fig. 2.

The effect of the water content in the powdered samples on the strength was investigated, and the results obtained are shown in Fig. 3. A maximum strength was obtained at a water content of about 10%.

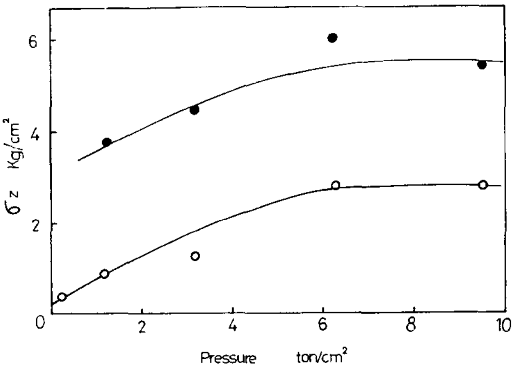

FIG. 1. Relationships between tensile strength and compacting pressure of alumina pellets: ○, sample I-1; ●, sample I-2.

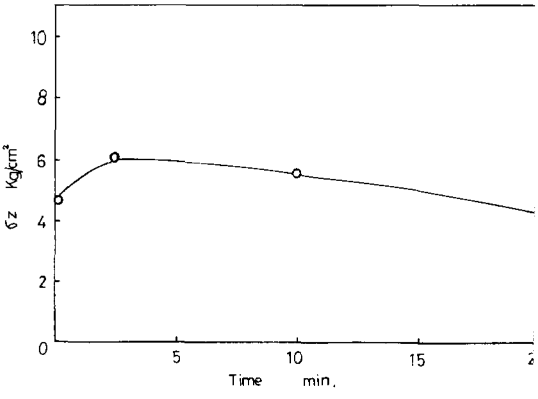

FIG. 2. Relationships between tensile strength and compacting time of alumina pellets: compacting pressure: 6400 kg/cm²; sample I-2.

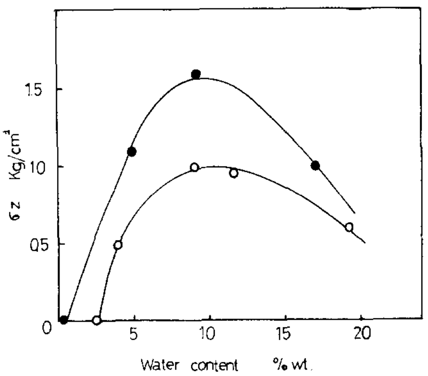

FIG. 3. Effect of water content in the alumina powder on the pellet strength: ○, sample II-1, ●, sample III-1; compacting pressure: 6400 kg/cm².

The strength decreased with an increase in water content up to 20%. In Fig. 4 the strength of sample I is plotted against the temperature of thermal decomposition between 150 and 800°C. Sample I-2 which was calcined at 400°C had the highest strength.

The influence of tableting on the pore structure and the catalytic activity was investigated for some samples. The effect of tableting on pore structure is shown for samples I and IV in Figs. 5 and 6, respectively. In Figs. 5A and 6A the cumulative pore volume is plotted against pore radius, while the distribution curves are shown in Figs. 5B and 6B. In the case of sample I, it is shown in Fig. 5B that small pores (<100 Å) were not affected by the compacting pressure up to 6000 kg/cm², but it is clear from Fig. 5A that the size of macropores larger than 1000 Å was decreased by the compression. On the other hand, in the case of sample IV prepared from the boehmite gel, a very broad pore size distribution ranging from about 300 to 37.5 Å was observed in the powdered form, as shown in Fig. 6B. By tableting this sample, however, the broad macropore distribution at 150–300 Å diminished and shifted to a smaller pore size (50 Å). The decrease of the volume of these macropores was observed as illustrated in Fig. 6A.

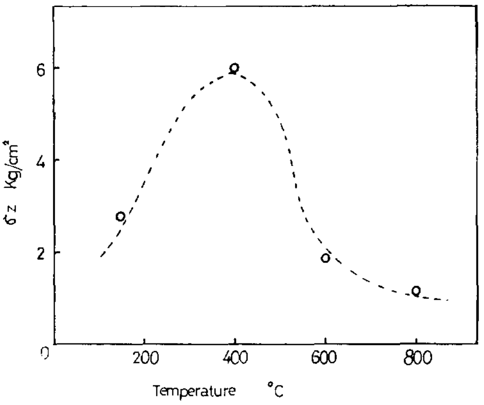

FIG. 4. Effect of heating temperature of alumina on the pellet strength: compacting pressure. 6400 kg/cm²; sample I.

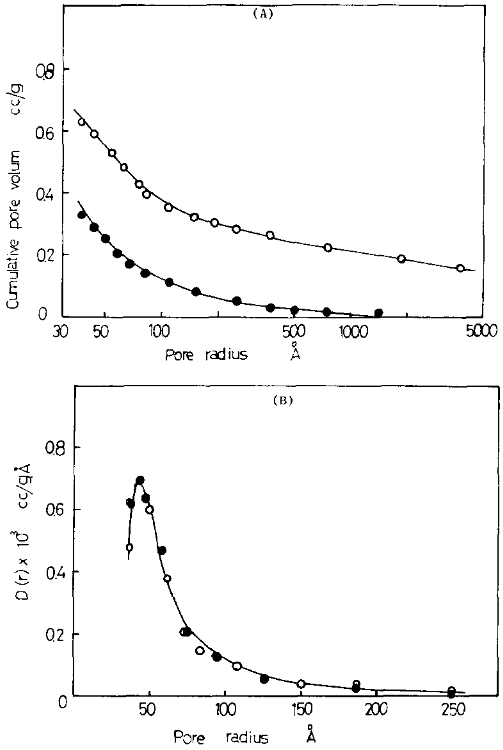

FIG. 5A. Effect of tableting on the pore volume distribution: ○, calcined powder of I-2; ●, calcined pellet of I-2; calcination at 500°C, compacting pressure: 6400 kg/cm². (B) Effect of tableting on the pore size distribution: same as (A).

The influence of pelletizing some of the samples on their catalytic activity is shown in Table 2. The difference in conversion of butene-1 to butene-2 (*cis* and *trans*), using powdered samples of II, III, and IV, was compared with that obtained using

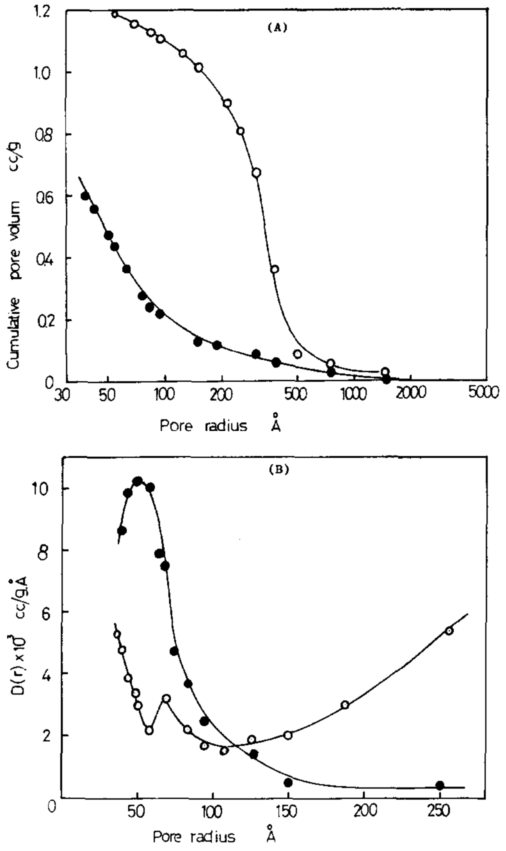

FIG. 6A. Effect of tableting on the pore volume distribution: ○, powder of IV; ●, pellet of IV; compacting pressure. 6400 kg/cm². (B) Effect of tableting on the pore size distribution: same as (A).

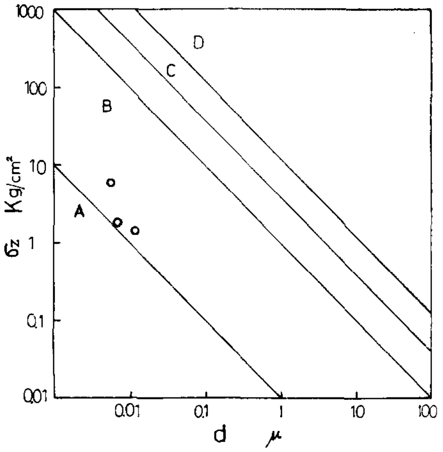

FIG. 7. Theoretical tensile strength of agglomerates and measured tensile strength of the alumina pellets: (A) van der Waals' force; (B) van der Waals' force with adsorption layer; (C) capillary force; (D) sintering.

pelleted samples of the same materials. As shown in Table 2 the catalytic activity and specific surface area were affected very little by the compression pressure up to 6400 kg/cm². Variation in starting material, however, did have an effect on these properties.

DISCUSSION

Many properties are required for a catalyst to be useful in industry. These factors

TABLE 2

EFFECT OF TABLETING ON THE POROUS STRUCTURE AND CATALYTIC ACTIVITY OF ALUMINAS

Porous structure and catalytic activity	Sample:	I-2	II-1	III-1
Surface area[a] (m² g⁻¹)	powder	283	337	258
	pellet[b]	261	317	237
Pore vol[c] (ml g⁻¹)	powder	0.34	0.45	0.42
	pellet	0.33	0.43	0.41
Catalytic activity[d] (% g⁻¹)	powder	1.9	2.1	3.3
	pellet	2.0	2.2	3.3

[a] BET area.

[b] Compacting pressure, 6400 kg/cm².

[c] Pore radius <300 Å.

[d] Conversion of butene-1 isomerization ($\% \ g_{cat}^{-1}$), reaction temp, 200°C; SV, 3480.

include, for example, high activity, good selectivity, high mechanical strength and duration of activity during use. In this study the mechanical strength of pelletized alumina catalyst has been investigated. Results of similar studies have also been reported in the literature (*6, 7*).

As was pointed out by Rumpf (*8*), the deviations of the measured values of tensile strength were not small. The maximum deviations obtained in this study were about 40%, and the deviations were partly due to the fact, that it was very difficult to control the pelletizing conditions precisely. It would be expected that the deviations could be reduced by better control of the pellet preparation technique prior to the measurement. A study is at present being carried out in this laboratory using an isostatic press to prepare the pellets. The minimum value of the tensile strength was selected from those measured, because this value should be directly correlated with the adhesion of powder from a scientific viewpoint. On the other hand, this value would also be important from a practical viewpoint, since it can be used as a measure of the mechanical strength of the industrial catalysts.

The difference between starting materials of alumina or alumina hydrate has an important effect upon the absolute values of the mechanical strength. However, as shown in Fig. 1, an increase in pellet strength was accompanied by an increase in the pelletizing pressure and this tendency was observed in every case. The maximum strength obtained and the pelletizing pressure required to obtain this maximum strength varied in a wide range for a variety of alumina or alumina hydrate starting materials as was shown in Table 3. Of the many factors which were examined to clarify the relation between the preparing conditions of pellets and the mechanical strength of pellets the preparing conditions of the starting materials were found to be the most important. Strictly speaking, the mechanical strength of the alumina pellets was affected more by the water content and the particle size of the alumina powder, than by the pelletizing conditions.

TABLE 3
The Maximum Tensile Strength Obtained and the Pelletizing Pressure of Various Alumina or Alumina Hydrate

Sample	Pelletizing pressure (kg/cm^2)	Max strength (kg/cm^2)
I-1	6400	2.4
I-2	6400	6.0
II-1	6400	1.6
III-1	6400	1.0
IV-1	5100	3.5

It was ascertained that the specific surface area and the catalytic activity of alumina for the selected reaction does not change by pelletizing under about 10000 kg/cm^2, but the distribution of macropore volume does. Therefore it can be concluded that during the pelletizing process for alumina catalyst larger particles move and smaller ones do not. The crystal or surface structure does not change, that is, the so-called "mechanochemical" reaction does not occur under the experimental conditions used in this research. These facts are due to the fibrous structure of alumina hydrates. This structure was observed by means of an electron microscope and X-ray small angle scattering to be an aggregate of ultimate particles whose diameter is 50–100 Å as was shown previously (*5*). In such an aggregate it seems difficult for the ultimate particles to move or to be destroyed during the application of a small pelletizing pressure of about 10000 kg/cm^2. As a result it is reasonable to observe no change of catalytic activity in this catalyst, while some catalysts change their activity by pelletizing.

Rumpf has recently published a paper on the mechanical strength of granules and agglomerates, and assuming the adhesion of powder particles by different bonding forces, proposed the following equation (*1*):

$$\sigma z = \frac{9}{8} \frac{(1 - e)}{\pi d^2} kH,$$

where σz, theoretical tensile strength; e, porosity; *d*, diameter of spherical particle; *k*, coordination number of particle; and *H*, adhesion force. His calculation was summarized in a figure as shown in Fig. 7, and it has been checked by his scientific associates (*9*). The values of the tensile strength of alumina pellets obtained in the present work are plotted in Fig. 7. These points are located in the region B, where the adhesion force by the van der Waals' interaction between adsorption layers operates. The amount of water adsorbed on the alumina surface during the measurement of the tensile strength was about 1–3 mmoles/g, this amount being that necessary, for the formation of a mono-molecular layer of water, which would be immovable. Therefore it is concluded, that the effect of the surface tension of the liquid water layer on the tensile strength of the alumina pellet is not as large as that of the van der Waals' interaction by the adsorbed layer. In addition it is shown that the mechanical strength of pellets prepared from some impregnated alumina is higher than for those prepared from pure alumina. For example, cobalt–molybdenum-impregnated alumina showed the highest value. The reason for this is not clear from this study, but it would be desirable to clarify this point in the near future.

When alumina is prepared by the calcination of macrocrystalline hydrate, small pores are formed by its dehydration and their distribution is very narrow (*5, 10, 11*). The pore size distribution of alumina prepared by decomposition from boehmite gel had a wide range to 100 Å, which may correspond to voids between irregularly agglomerating particles, that is, ultimate and/or aggregating ones, and the pore structure does not change before and after calcination (*5, 11*). Johnson and Mooi (*11*) observed the pore size distribution of alumina powder obtained from the mixture of trihydrate and boehmite and found that pores larger than 100 Å were affected by the compaction during the pelletizing process. In this study it has been shown that the pore volume distribution formed by larger particles is affected by pelletizing. Such a phenomenon has been observed on pelletizing of a zinc oxide-chromia catalyst by one of the authors.

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